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(54) Curable organosiloxane composition.

(57) Curable organosiloxane compositions exhibiting superior adhesion to a variety of substrates in the cured form comprise a polyorganosiloxane containing at least two alkenyl radicals per molecule, an organohydrogensiloxane, a platinum-containing catalyst and, as the adhesion promoter, the combination of 1) an organosilicon material containing diorganovinylsiloxy, triorganosiloxy, SiO₄ and alkoxy groups in specified proportions and 2) a silane containing at least two alkoxy groups and either a glycidoxo or epoxycyclohexyl group bonded to silicon.

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CURABLE ORGANOSILOXANE COMPOSITION

The present invention relates to a curable polyorganosiloxane composition. More specifically, the present invention relates to a curable polyorganosiloxane composition which bonds well to substrates in contact with said composition during curing.

Many methods have been proposed for imparting adhesion to organosiloxane compositions that cure by the addition reaction of lower alkenyl radicals with silicon-bonded hydrogen atoms in the presence of a platinum catalyst. Some of these methods involve addition of various types of adhesion promoters to the compositions. The addition of a silane containing both alkenyl radicals and silicon-bonded alkoxy groups or a partial hydrolysis product of the silane is taught in United States Patent No. 4,169,273, which issued to Imai and Tanaka on April 1, 1980, United States Patent No. 4,329,273, which issued to Hardman et al. on May 11, 1982, and in Japanese Patent Publication No. 76/28309. The use as adhesion promoters of silanes containing both silicon-bonded hydrogen atoms and silicon-bonded alkoxy groups and partial hydrolysis products of these silanes is described in Japanese Patent Publication 82/5836. Curable compositions wherein the adhesion promoter is a linear or cyclic polyorganosiloxane wherein each molecule contains substituents selected from at least one member of the group consisting of lower alkenyl, silicon-bonded hydrogen, silicon-bonded alkoxy, alkoxysilylalkyl, epoxy and ester are described in United States Patent No. 3,669,072, which issued to Clark and Hayes on October 17, 1972, United States Patent No. 4,082 726, which issued to Mine et al. on April 4, 1978, Japanese patent publication 80/39258, and Japanese published application (Kokai) Nos. 54/58755 and 54/58756. The use of an isopropenoxysilane or partial hydrolyzate thereof as an

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1 adhesion promoter is disclosed in United States Patent No.
3,892,707, which issued to Itoh and Harada on July 1, 1975.

Each of the aforementioned prior art adhesion
promoters has disadvantages associated with its use. The
5 presence of both a lower alkenyl radical and an alkoxy group
in a single silane interferes with the addition reaction and
slows the cure rate. Siloxanes containing epoxy or ester
groups are not completely miscible the principal siloxane
ingredient, and the composition becomes cloudy following the
10 addition. Trimethoxysilane is an extremely toxic material.
The synthesis of lower alkenoxysilanes is both costly and
time consuming, and the silanes tend to be scattered during
reduced pressure degassing of the polyorganosiloxane
composition. Furthermore, all of these additive methods
15 suffer from the problem that a curing temperature of 100°C
or higher is usually needed in order to generate
adhesiveness.

United States Patent No. 4,087,585, which issued
to Schulz on May 2, 1978 discloses adhesion promoters for
20 curable compositions obtained by blending a vinyl-containing
polyorganosiloxane, an organosilicon compound containing
silicon bonded hydrogen atoms and a platinum catalyst. The
adhesion promoter consists essentially of the combination of
an epoxy-containing alkoxysilane with a polyorganosiloxane
25 containing at least one silicon bonded hydroxyl radical and
at least one silicon bonded vinyl radical.

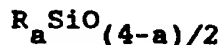
Japanese Patent Application No.168272/85, filed in
the name of the same inventor as the present application,
teaches using a specified class of organosilicon compounds
30 as the adhesion promoter for organosiloxane compositions
curable by a platinum catalyzed hydrosilation reaction. The
organosilicon compounds contain diorganovinylsiloxy,
triorganosiloxy, $\text{SiO}_{4/2}$ and alkoxy units in specified molar
ratios.

1 Further study by the present inventor with a view
to improving the adhesion of compositions curable by a
platinum-catalyzed hydrosilation reaction resulted in the
finding that superior adhesion can be achieved by combining
5 the organosilicon compounds disclosed in the aforementioned
Japanese Patent Application No. 168272/85 with an
epoxy-substituted alkoxysilane.

One object of the present invention is to provide a
curable polyorganosiloxane composition which bonds even more
10 tightly to diverse substrates, and particularly to various
organic resin substrates, due to the addition of a specific
adhesion promoter.

This invention provides a curable composition
comprising:

15 (A) a polyorganosiloxane with the average unit formula



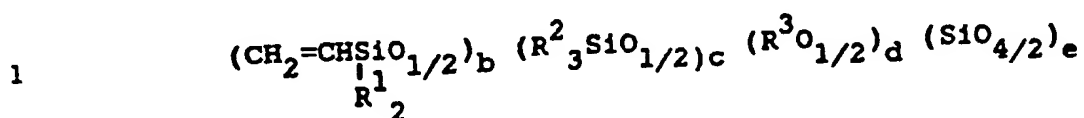
containing an average of at least two lower alkenyl groups
per molecule, where R represents a monovalent hydrocarbon
20 group and the value of a is from 0.8 to 2.2;

(B) an organohydrogensiloxane containing at least 2 silicon-
bonded hydrogen atoms per molecule and no alkenyl groups,
where the concentration of (B) is sufficient to provide a
25 molar ratio of silicon bonded hydrogen atoms relative to the
total moles of alkenyl groups present in ingredients A and D
of from 0.5 to 3.0.

(C) a amount of a platinum-type catalyst equivalent to from
0.1 to 100 ppm of platinum metal, based on the combined
30 quantities of ingredients (A), (B) and (C); and

(D) a mixture or reaction product of (a) a polysiloxane
corresponding to the average formula

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5 where R^1 , R^2 and R^3 represent identical or different monovalent hydrocarbon radicals other than alkenyl radicals and contain from 1 to 3 carbon atoms, b and d are at least 1, c is 0 or greater, the value of $(b + c)/d$ is from 0.2 to 2, the value of $(b + c + d)/e$ is from 0.4 to 4 and e is less than 30 and (b) an alkoxysilane of the formula



15 where A represents a glycidoxy or epoxycyclohexyl group, R^4 represents a divalent hydrocarbon radical containing from 1 to 3 carbon atoms, R^5 and R^6 represent identical or different monovalent hydrocarbon radicals other than alkenyl and contain from 1 to 3 carbon atoms, and n is 1 or 0, and where the weight ratio of (a) to (b) is from 0.1 to 10, inclusive and the weight ratio of (D) relative to (A) does not exceed 0.2.

25 By way of explanation of the present invention, ingredient A is the principal ingredient of the present compositions. This ingredient, an ethylenically unsaturated polyorganosiloxane, undergoes an addition reaction and crosslinks with ingredient B, an organohydrogensiloxane, in the presence of a platinum-containing catalyst, ingredient C. The lower alkenyl groups present in ingredient A are exemplified by vinyl, allyl and propenyl. The lower alkenyl groups may be present at any position in the molecule, but are preferably present at least at the terminal positions of the molecule.

30 The monovalent hydrocarbon radicals represented by R are exemplified by alkyl such as methyl, ethyl, propyl and butyl; aryl such as phenyl and tolyl; benzyl; haloalkyl

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1 groups such as chloropropyl and trifluoropropyl; and the
above-mentioned alkenyl radicals. In addition to R, small
amounts of hydroxyl groups may be present. Preferably at
least 70% of the R radicals are methyl in order to achieve
5 excellent bonding with the substrate. Most preferably at
least 90% of the R radicals are methyl in order to obtain
an excellent transparency. The average value of α is from
0.8 to 2.2, but is preferably from 1.95 to 2.05 to achieve
excellent bonding.

10 The molecular configuration of ingredient A can be
straight chain, branch-containing straight chain, cyclic,
network or three-dimensional, however a straight-chain
structure, possibly with a very small quantity of branching,
is preferred. The molecular weight of this component is not
15 particularly limited, and may range from that of a
low-viscosity liquid to that equivalent to a very
high-viscosity gum. The viscosity of this ingredient
component is preferably 0.05 to 100 Pa.s, measured at 25°C
from a consideration of the workability of the composition
20 in mixing and bonding.

Examples of polyorganosiloxanes suitable as
ingredient A include but are not limited to
polyvinylsiloxane, vinylsiloxane-methylsiloxane copolymers,
dimethylvinylsiloxyl terminated polydimethylsiloxanes,
25 dimethylvinylsiloxyl-terminated
dimethylsiloxane-methylphenylsiloxane copolymers,
dimethylvinylsiloxyl-terminated
dimethylsiloxane-methylvinylsiloxane copolymers,
dimethylvinylsiloxyl-terminated dimethylsiloxane-
30 diphenylsiloxane-methylvinylsiloxane copolymers,
trimethylsiloxyl-terminated dimethylsiloxane-methylvinyl-
siloxane copolymers, trimethylsiloxyl-terminated
dimethylsiloxane-methylphenylsiloxane-methylvinylsiloxane
copolymers, dimethylvinylsiloxyl-terminated
35 polymethyl(3,3,3-trifluoropropyl) siloxanes,

1 dimethylvinylsiloxy-terminated
dimethylsiloxy-methyl(3,3,3-tri-fluoropropyl)siloxane
copolymers and polysiloxanes composed of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$
units, $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units.

5 The combination of a
dimethylvinylsiloxy-terminated polydiorganosiloxane with a
polysiloxane composed of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$ units,
 $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units can be used as
ingredient A when an increased strength is sought for the
10 cured product of the present polyorganosiloxane
compositions.

Ingredient B is the crosslinking agent for
ingredient A. The silicon-bonded hydrogen atoms of this
ingredient participate in an addition reaction with the
15 lower alkenyl radicals ingredient A under the catalytic
activity of ingredient C in order to cure the composition.
The organic groups bonded to silicon are typically
monovalent hydrocarbon radicals, and preferred examples are
as enumerated for R above, with the exception of alkenyl
20 radicals. The molecular configuration of the
organohydrogensiloxane is not particularly restricted and it
may be straight chain, branch-containing straight chain or
cyclic. The molecular weight of this ingredient is likewise
not particularly restricted, however the viscosity is
25 preferably from about 0.001 to about 50 Pa.s at 25°C to
obtain an excellent miscibility with ingredient A. The
concentration of this ingredient in the present compositions
is determined by the condition that the molar ratio of the
total quantity of silicon-bonded hydrogen atoms of this
30 ingredient relative to the total quantity of alkenyl groups
in ingredients A and D is from 0.5 to 3, inclusive. When
this molar ratio is less than 0.5, an excellent curability
will not be obtained. When this ratio exceeds 3.0 the
resulting composition tends to foam easily.

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1 When the aforementioned vinyl-containing
polysiloxane is additionally employed for reinforcement or
other purposes, additional organohydrogensiloxane must be
present to maintain the required molar ratio of silicon
5 bonded hydrogen to alkenyl radicals in the composition.

Specific examples of the organohydrogensiloxane
ingredient include but are not limited to
trimethylsiloxy-terminated polymethylhydrogensiloxanes,
trimethylsiloxy-terminated dimethylsiloxane-methylhydrogen-
10 siloxane copolymers,
dimethylhydrogensiloxy-terminated polymethylhydrogen-
siloxanes,
dimethylhydrogensiloxy-terminated dimethylsiloxane-
methylhydrogensiloxane copolymers,
15 dimethylsiloxane-methylhydrogensiloxane cyclic copolymers,
copolymers composed of $(\text{CH}_3)_2\text{HSiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units
and copolymers composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units, $(\text{CH}_3)_2\text{HSiO}_{1/2}$
units and $\text{SiO}_{4/2}$ units.

Ingredient C catalyzes the addition reaction of
20 silicon-bonded hydrogen atoms with alkenyl radicals and its
concrete examples include chloroplatinic acid, alcohol and
ketone solutions of chloroplatinic acid, aged alcohol and
ketone solutions of chloroplatinic acid, chloroplatinic
acid-olefin complexes, chloroplatinic acid-alkenylsiloxane
25 complexes, platinum-diketone complexes, platinum black and
supported platinum.

The concentration of ingredient C is equivalent to
from 0.1 to 100 ppm of platinum metal based on the combined
weight quantity of ingredients A, B, C and D. The
30 crosslinking reaction will not proceed adequately at below
0.1 ppm of platinum in the composition. The use of more
than 100 ppm of platinum is uneconomical and also
significantly reduces the working time of the present
curable compositions at room temperature. The platinum
35 concentration is typically from about 1 to about 20 ppm.

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1 The presence of ingredient D distinguishes the
present compositions from prior art materials. This
ingredient is responsible for the excellent bonding to
substrates with which the present compositions are in
contact with during curing.

5 Part (a) of ingredient D is a polysiloxane with a
three-dimensional structure in which the basic structural
unit is the $\text{SiO}_{4/2}$ unit. This unit is bonded through its
oxygen atoms to the $\text{CH}_2=\text{CH}(\text{R}^1)_2\text{Si}$, R^2_3Si and R^3 groups.
10 This ingredient contains fewer than 30 $\text{SiO}_{4/2}$ units because
above this limit the molecular weight is too large for the
ingredient to impart the required adhesion to the
composition. The number of $\text{SiO}_{4/2}$ units is preferably about
20 from the standpoint of the miscibility of this ingredient
15 with ingredient A, but must be at least 3 to prevent
volatilization of part (a) during degassing of the
composition.

The values represented by b and d in the formula
for part (a) are both at least 1 because an excellent
adhesion cannot be generated when these values are less than
20 1. The value of c can be 0 or greater, the value of $(\underline{b} + \underline{c})/\underline{d}$
is from 0.2 to 2, and the value represented by $(\underline{b} + \underline{c} + \underline{d})/\underline{e}$
must be from 0.4 to 4. The reason for these limits is
that excellent adhesion cannot be imparted when these values
25 fall outside the specified ranges. It has been found that a
composition in which $(\underline{b} + \underline{c} + \underline{d})/\underline{e}$ exceeds 4 essentially
cannot be produced. R^1 , R^2 and R^3 are individually
identical or different monovalent hydrocarbon radicals
containing from 1 to 3 carbon atoms, with the proviso that
these radicals do not contain ethylenic unsaturation. R^1 and
30 R^2 are preferably methyl and R^3 is preferably methyl or
ethyl.

Part (b) of ingredient D is an alkoxysilane
containing at least one epoxide group. Specific examples of
this ingredient include but are not limited to

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1 gamma-glycidoxypropyltrimethoxysilane,
gamma-glycidoxypropylmethyldimethoxysilane,
3,4-epoxycyclohexylethyltrimethoxysilane and
3,4-epoxycyclohexylethylmethyldimethoxysilane.

5 Part (a) of ingredient D can be synthesized by
methods known in the art. An example of such a method is
the cohydrolysis of 1 or more of dimethylvinylchlorosilane,
dimethylvinylacetoxysilane, dimethylvinylethoxysilane,
divinyldimethyltetramethyldisiloxane, trimethylchlorosilane,
10 trimethylacetoxysilane and hexamethyldisiloxane with methyl
orthosilicate or ethyl orthosilicate in the presence of a
strictly regulated quantity of water. It is recommended
that an acid catalyst such as hydrochloric acid be employed
in this cohydrolysis. Each silicon compound used in this
15 cohydrolysis can be a mixture of 2 or more species.

A compound corresponding to part (a) produced as
described hereinbefore may contain residual silanol groups
and, after mixing with part (b), an alcohol-releasing
reaction may be conducted in the presence of an alkali
20 catalyst such as sodium hydroxide, potassium hydroxide or
potassium silanolate. During the preparation of ingredient
D, part (a) may be partially reacted with part (b), or a
simple mixture of these two parts may be used.

When the alkali-catalyzed alcohol releasing
25 reaction is performed, the mixture present following the
reaction is preferably neutralized with, for example,
carbon dioxide, a chlorosilane or acetic acid, before use.
The weight ratio of part (a) to part (b) in ingredient D
must be within the range of 0.1 to 10, and preferably within
30 the range of from 0.5 to 2 in order to obtain good adhesion
between the cured composition of this invention and the
substrate.

The weight of ingredient D must not exceed 1/5 of
the weight of ingredient A because the addition of larger
35 quantities degrades the properties of the composition

1 itself. The optimal quantity of ingredient D for obtaining
excellent adhesion will depend on the structures of the
other components, but it is approximately from 1 to 8 parts
by weight of ingredient D per 100 parts by weight of
5 ingredient A.

The curable polyorganosiloxane compositions of the
present invention can be produced by simply mixing
ingredients A, B, C, and D using any mixing apparatus
suitable for mixing a fluid or gum. Examples of suitable
10 mixing devices include planetary mixers, screw mixers,
static mixers and kneader mixers.

It is recommended that a small or very small
amount of an additive, such as acetylene compounds,
hydrazines, triazoles, phosphines and mercaptans, be added
15 to the curable polyorganosiloxane composition of the present
invention in order to inhibit the curing reaction at room
temperature. In addition, fillers such as fine silica
powder and carbon black, thermal stabilizers, colorants and
flame retardants may optionally be added unless they
20 adversely affect achieving the objectives of the present
invention, specifically a curable composition exhibiting
excellent adhesion to a variety of substrates.

The following examples describe preferred
embodiments of the present compositions and should not be
25 interpreted as limiting the scope of the accompanying
claims. All parts and percentages in the examples are by
weight unless otherwise specified, and viscosity and other
properties are measured at 25°C.

Example 1

30 A series of polyorganosiloxane compositions were
prepared from a dimethylvinylsiloxy-terminated
polydimethylsiloxane with a viscosity of 2 Pa.s (polymer
A1); a trimethylsiloxy-terminated copolymer consisting
essentially of dimethylsiloxane and methylhydrogensiloxane
35 units in a molar ratio of 3:5, respectively, and exhibiting

1 a viscosity of 0.01 Pa.s (polymer X1); a 1% by weight
 solution of chloroplatinic acid in 2-ethylhexanol (catalyst
 1); a polysiloxane (polymer M1) with the formula

$$[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}]_4 [(\text{CH}_3)_3\text{SiO}_{1/2}]_4 [\text{CH}_3\text{O}_{1/2}]_{12} [\text{SiO}_{4/2}]_{12};$$
 5 a polysiloxane (polymer M2) with the formula

$$[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}]_5 [(\text{CH}_3)_3\text{SiO}_{1/2}]_4 [\text{CH}_3\text{O}_{1/2}]_9 [\text{SiO}_{4/2}]_{11};$$
 a polysiloxane (polymer M3) with the formula

$$[\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}]_4 [(\text{CH}_3)_3\text{SiO}_{1/2}]_6 [\text{CH}_3\text{O}_{1/2}]_6 [\text{SiO}_{4/2}]_{10};$$
 gamma-glycidoxypropyltrimethoxysilane (silane 1); the reaction
 10 product (polymer M4) obtained by heating a 1:1 weight ratio
 mixture of polymer M1 and silane 1 at 100°C for 1 hour in the
 presence of 500 ppm KOH, removing the produced methanol and
 neutralizing the reaction mixture with Me_3SiCl ; the reaction
 mixture (polymer M5) obtained by heating a 1:1 weight ratio
 15 mixture of polymer M2 and silane 1 at 100°C for one hour in
 the presence of 500 ppm KOH; and 3-methylbutyne-3-ol (additive
 I1). Each composition was cured in contact with glass at
 150°C. The light transmission and adhesion to glass of the
 cured products were measured and the results are reported in
 20 Table 1. The adhesion values reported in Table 1 are the %
 cohesive failure, i.e. the percent of substrate surface to
 which the cured elastomer had adhered. The curing time is the
 time required for a complete curing of the composition. Light
 transmission was measured at a wavelength of 500 nm on a 10 mm
 25 thickness of the cured product.

30

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TABLE I

Ingredients	Comparative example 1	Present invention						
		2	3	4	5	6	7	8
polymer A1 (parts)	100	100	100	100	100	100	100	100
polymer X1 (parts)	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
catalyst 1 (parts)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
additive I1 (parts)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
polymer M1 (parts)	1.5	1.5	1.5					
polymer M2 (parts)				1.5				
polymer M3 (parts)					2.0	1.0		
polymer M4 (parts)							3.0	
polymer M5 (parts)								3.0
silane 1 (parts)		1.5	1.0	1.5	1.0	2.0		
light transmission (%)	98	98	98	98	97	98	98	98
curing time (minutes @150°C)	3	3	3	3	3	3	3	3
Cohesive Failure (%)	60	100	100	100	100	100	100	100

Example 2

1 A composition was prepared from 100 parts
dimethylvinylsiloxy-terminated polydimethylsiloxane with a
viscosity of 10 Pa.s; 10 parts polyorganosiloxane resin with
5 a vinyl group content of 1%, a softening point of 120°C and
consisting essentially of dimethylvinylsiloxy,
trimethylsiloxy and $\text{SiO}_{4/2}$ units; 30 parts of
trimethylsilyl-hydrophobicized fumed silica; 0.4 parts
tetramethyltetravinylcyclotetrasiloxane; 10 parts of a
10 trimethylsiloxy-terminated copolymer consisting essentially
of dimethylsiloxane and methylhydrogensiloxane units in a
molar ratio of 3:1, respectively, and exhibiting a viscosity
of 0.01 Pa.s; and a divinyltetramethyl-
15 disiloxane-chloroplatinic acid complex in an amount
equivalent to 10 ppm platinum, based on the weight of the
total composition. These ingredients are combined and
blended with one of the adhesion promoters from Example 1,
in the quantity specified in Table 2, followed by degassing
at room temperature under reduced pressure for 30 minutes.
20 The compositions were then applied to various substrates and
cured at 120°C for 30 minutes. The percent cohesive failure
was measured for each substrate and the results reported in
Table 2. In the table, the concentrations of the adhesion
promoters are expressed in parts by weight, based on 100
25 parts of the polydimethylsiloxane.

30

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Table 2

Example No.	25	9*	10	11	12	1
			Adhesion Promoters			
Substrates	A	B	C	D		
iron	50	95	50	50	50	
stainless steel	50	95	50	50	50	
copper	100	100	100	100	100	
aluminum	100	100	100	100	100	
phenol resin	100	100	100	100	100	
polyethylene terephthalate resin	100	100	100	100	100	
epoxy resin	0	100	100	100	100	
polybutylene terephthalate resin	100	100	100	100	100	
polymethyl methacrylate resin	50	100	100	100	100	
polyphenylene sulfide resin	0	100	100	100	100	

Adhesion Promoters: A - 3 parts polymer M1 (Ex.1)
 B - 3 parts of a 1:1 weight ratio mixture of polymer M1 and silane 1
 C - 3 parts polymer M4
 D - 3 parts polymer M5

* - Comparative Example

1 The foregoing data demonstrate that the addition
of the present adhesion promoters to an addition-curable
polyorganosiloxane composition imparts excellent adhesion
without adversely affecting other desirable properties such
5 as rate of the curing reaction, transparency. In addition
there is no reduction in adhesion following degassing of the
composition. The compositions therefore exhibit excellent
adhesion to substrates, in particular, organic resins, which
are in contact with the composition during curing.

10 Accordingly, the curable polyorganosiloxane
compositions of this invention are suitable as adhesives or
coating materials for diverse substrates, for example,
glass, ceramics, metals, resins, papers and textiles. The
compositions are useful in various industries such as the
15 electric/electronic industry, the measurement instrument
industry, the automobile industry, the machine industry, in
civil engineering and construction and in the container,
packaging and medical appliance industries.

20 In addition, the composition is highly transparent
and so is optimal as an adhesive in optical applications.

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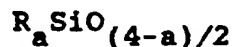
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1 Claims:

1. A curable composition comprising:

(A) a polyorganosiloxane with the average unit formula



5 containing an average of at least two lower alkenyl groups per molecule, where R represents a monovalent hydrocarbon group and the value of a is from 0.8 to 2.2;

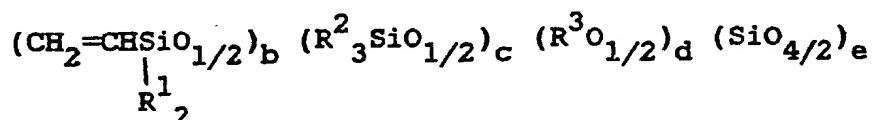
(B) an organohydrogensiloxane containing at least 2 silicon-bonded hydrogen atoms per molecule and no alkenyl groups, where the concentration of (B) is sufficient to provide a molar ratio of silicon bonded hydrogen atoms relative to the total moles of alkenyl groups present in ingredients A and D of from 0.5 to 3.0.

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(C) a amount of a platinum-type catalyst equivalent to from 0.1 to 100 ppm of platinum metal, based on the combined quantities of ingredients (A), (B) and (C); and

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(D) a mixture or reaction product of (a) a polysiloxane corresponding to the average formula

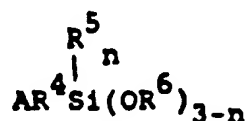


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where R^1 , R^2 and R^3 represent identical or different monovalent hydrocarbon radicals other than alkenyl radicals and contain from 1 to 3 carbon atoms, b and d are at least 1, c is 0 or greater, the value of $(\underline{b} + \underline{c})/\underline{d}$ is from 0.2 to 2, the value of $(\underline{b} + \underline{c} + \underline{d})/\underline{e}$ is from 0.4 to 4 and e is less than 30 and (b) an alkoxysilane of the formula

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5 where A represents a glycidoxy or epoxycyclohexyl group, R⁴ represents a divalent hydrocarbon radical containing from 1 to 3 carbon atoms, R⁵ and R⁶ represent identical or different monovalent hydrocarbon radicals other than alkenyl and contain from 1 to 3 carbon atoms, and n is 1 or 0, and where the weight ratio of (a) to (b) is from 0.1 to 10, inclusive and the weight ratio of (D) relative to (A) does not exceed 0.2.

15 2. A composition according to claim 1 where R is alkyl, aryl, haloalkyl or alkenyl, the hydrocarbon radicals present in (B) are alkyl, aryl or haloalkyl, the molar ratio of silicon bonded hydrogen atoms to alkenyl radicals in said composition is from 0.5 to 30, inclusive, R¹ and R² are methyl and R³ is methyl or ethyl.

20 3. A composition according to claim 2 where R is methyl or 3,3,3-trifluoropropyl, the alkenyl radicals are vinyl, and part (b) of ingredient D is selected from the group consisting of gamma-glycidoxypropyltrimethoxysilane, gamma-glycidoxymethyldimethoxysilane, 25 3,4-epoxycyclohexylethyltrimethoxysilane, and 3,4-epoxycyclohexylethylmethyldimethoxysilane.

30 4. A composition according to claim 3 where at least 70 percent of the R radicals are methyl, a is no more than 20, the composition contains from 1 to 8 parts by weight of (D) per 100 parts of (A), and the weight ratio of part (a) of ingredient (D) to part (b) of ingredient (D) is from 0.5 to 2.

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5. A composition according to claim 4 where at least 90 percent of the radicals represented by R are methyl, the value of a is from 1.95 to 2.05, the viscosity of (A) is from 0.05 to 100 Pa.s, the viscosity of (B) is from 0.001 to 50 Pa.s, the concentration of said catalyst is equivalent to from 1 to 20 ppm of platinum, based on the weight of said composition, the composition contains a polysiloxane consisting essentially of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$, $(\text{CH}_3)_3\text{SiO}_{1/2}$ and $\text{SiO}_{4/2}$ units, and a platinum catalyst inhibitor.

6. A composition according to claim 5 where the platinum catalyst is chloroplatinic acid, b is 4 or 5, c is 4, 5, or 6, the value of d is from 6 to 12, inclusive, the value of e is 10, 11 or 12, part (b) of ingredient (D) is gamma- glycidoxypropyltrimethoxysilane and the weight ratio of part (a) to part (b) of ingredient (D) is 1:1.

7. A composition according to claim 6 where ingredient (D) is a reaction product of part (a) and part (b) of ingredient (D).

8. A composition according to claim 7 where said composition contains fume silica as a filler.

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(54) Curable organosiloxane composition.

(57) Curable organosiloxane compositions exhibiting superior adhesion to a variety of substrates in the cured form comprise a polyorganosiloxane containing at least two alkenyl radicals per molecule, an organohydrogensiloxane, a platinum-containing catalyst and, as the adhesion promoter, the combination of 1) an organosilicon material containing diorganovinylsiloxy, triorganosiloxy, $\text{SiO}_{4/2}$ and alkoxy groups in specified proportions and 2) a silane containing at least two alkoxy groups and either a glycidioxy or epoxycyclohexyl group bonded to silicon.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86117116.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D, A	<u>US - A - 4 082 726</u> (MINE et al.) * Claims 1,3-9; examples 2,3 *	1,2,8	C 08 L 83/07// (C 08 L 83/07 C 08 L 83:05 C 08 L 83:07 C 08 K 5/54)
D, A	<u>US - A - 4 087 585</u> (SCHULZ) * Claims 1-6,11 *	1-3,5, 8	
D, A	<u>US - A - 4 196 273</u> (IMAI et al.) * Claims 1,2; example 4 *	1,2,5, 8	
A	<u>US - A - 3 699 073</u> (WADA et al.) * Claims 1,2; example 6 *	1,2,5, 8	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 L 83/00 C 08 K
Place of search VIENNA		Date of completion of the search 22-02-1990	Examiner KALTENEGGER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

(19)



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US-A- 3 699 073
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US-A- 4 087 585
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Description

The present invention relates to a curable polyorganosiloxane composition. More specifically, the present invention relates to a curable polyorganosiloxane composition which bonds well to substrates in contact with said composition during curing.

Many methods have been proposed for imparting adhesion to organosiloxane compositions that cure by the addition reaction of lower alkenyl radicals with silicon-bonded hydrogen atoms in the presence of a platinum catalyst. Some of these methods involve addition of various types of adhesion promoters to the compositions. The addition of a silane containing both alkenyl radicals and silicon-bonded alkoxy groups or a partial hydrolysis product of the silane is taught in United States Patent No. 4,196,273, which issued to Imai and Tanaka on April 1, 1980, United States Patent No. 4,329,273, which issued to Hardman et al. on May 11, 1982, and in Japanese Patent Publication No. 76/28309. The use as adhesion promoters of silanes containing both silicon-bonded hydrogen atoms and silicon-bonded alkoxy groups and partial hydrolysis products of these silanes is described in Japanese Patent Publication 82/5836. Curable compositions wherein the adhesion promoter is a linear or cyclic polyorganosiloxane wherein each molecule contains substituents selected from at least one member of the group consisting of lower alkenyl, silicon-bonded hydrogen, silicon-bonded alkoxy, alkoxysilylalkyl, epoxy and ester are described in United States Patent No. 3,699,072, which issued to Clark and Hayes on October 17, 1972, United States Patent No. 4,082 726, which issued to Mine et al. on April 4, 1978, Japanese patent publication 80/39258, and Japanese published application (Kokai) Nos. 54/58755 and 54/58756. The use of an isopropenoxysilane or partial hydrolyzate thereof as an adhesion promoter is disclosed in United States Patent No. 3,892,707, which issued to Itoh and Harada on July 1, 1975.

Each of the aforementioned prior art adhesion promoters has disadvantages associated with its use. The presence of both a lower alkenyl radical and an alkoxy group in a single silane interferes with the addition reaction and slows the cure rate. Siloxanes containing epoxy or ester groups are not completely miscible the principal siloxane ingredient, and the composition becomes cloudy following the addition. Trimethoxysilane is an extremely toxic material. The synthesis of lower alkenoxysilanes is both costly and time consuming, and the silanes tend to be scattered during reduced pressure degassing of the polyorganosiloxane composition. Furthermore, all of these additive methods suffer from the problem that a curing temperature of 100 °C or higher is usually needed in order to generate adhesiveness.

United States Patent No. 4,087,585, which issued to Schulz on May 2, 1978 discloses adhesion promoters for curable compositions obtained by blending a vinyl-containing polyorganosiloxane, an organosilicon compound containing silicon bonded hydrogen atoms and a platinum catalyst. The adhesion promoter consists essentially of the combination of an epoxy-containing alkoxysilane with a polyorganosiloxane containing at least one silicon bonded hydroxyl radical and at least one silicon bonded vinyl radical.

Japanese Patent Application No. 168272/85, filed in the name of the same inventor as the present application, teaches using a specified class of organosilicon compounds as the adhesion promoter for organosiloxane compositions curable by a platinum catalyzed hydrosilation reaction. The organosilicon compounds contain diorganovinylsiloxy, triorganosiloxy, SiO₄/2 and alkoxy units in specified molar ratios.

Further study by the present inventor with a view to improving the adhesion of compositions curable by a platinum-catalyzed hydrosilation reaction resulted in the finding that superior adhesion can be achieved by combining the organosilicon compounds disclosed in the aforementioned Japanese Patent Application No. 168272/85 with an epoxy-substituted alkoxysilane.

One object of the present invention is to provide a curable polyorganosiloxane composition which bonds even more tightly to diverse substrates, and particularly to various organic resin substrates, due to the addition of a specific adhesion promoter.

This invention provides a curable composition comprising:

(A) a polyorganosiloxane with the average unit formula

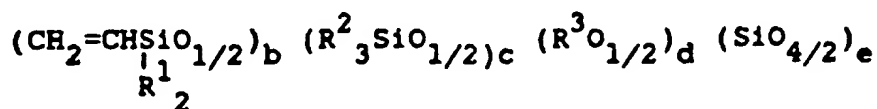


containing an average of at least two radicals selected from the group consisting of vinyl, allyl, propenyl per molecule, where R represents a monovalent hydrocarbon group a haloalkyl group, a hydroxy group or the above-mentioned alkenyl radicals and the value of a is from 0.8 to 2.2;

(B) an organohydrogensiloxane containing at least 2 silicon-bonded hydrogen atoms per molecule and no alkenyl groups, where the concentration of (B) is sufficient to provide a molar ratio of silicon bonded hydrogen atoms relative to the total moles of alkenyl groups present in ingredients A and D of from 0.5 to 3.0.

- (C) a amount of a platinum-type catalyst equivalent to from 0.1 to 100 ppm of platinum metal, based on the combined quantities of ingredients (A), (B) and (C); and
 (D) a mixture or reaction product of (a) a polysiloxane corresponding to the average formula

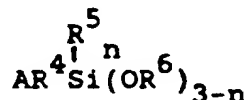
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where R^1 , R^2 and R^3 represent identical or different monovalent hydrocarbon radicals other than alkenyl radicals and contain from 1 to 3 carbon atoms, b and d are at least 1, c is 0 or greater, the value of $(b + c)/d$ is from 0.2 to 2, the value of $(b + c + d)/e$ is from 0.4 to 4 and e is from 3 to 30 and (b) an alkoxysilane of the formula

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where A represents a glycidoxy or epoxycyclohexyl group, R^4 represents a divalent hydrocarbon radical containing from 1 to 3 carbon atoms, R^5 and R^6 represent identical or different monovalent hydrocarbon radicals other than alkenyl and contain from 1 to 3 carbon atoms and n is 1 or 0, and where the weight ratio of (a) to (b) is from 0.1 to 10, inclusive and the weight ratio of (D) relative to (A) does not exceed 0.2.

25

By way of explanation of the present invention, ingredient A is the principal ingredient of the present compositions. This ingredient, an ethylenically unsaturated polyorganosiloxane, undergoes an addition reaction and crosslinks with ingredient B, an organohydrogensiloxane, in the presence of a platinum-containing catalyst, ingredient C. The lower alkenyl groups present in ingredient A are exemplified by vinyl, allyl and propenyl. The lower alkenyl groups may be present at any position in the molecule, but are preferably present at least at the terminal positions of the molecule.

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The monovalent hydrocarbon radicals represented by R are exemplified by alkyl such as methyl, ethyl, propyl and butyl; aryl such as phenyl and tolyl; benzyl; haloalkyl groups such as chloropropyl and trifluoropropyl; and the above-mentioned alkenyl radicals. In addition to R, small amounts of hydroxyl groups may be present. Preferably at least 70% of the R radicals are methyl in order to achieve excellent bonding with the substrate. Most preferably at least 90% of the R radicals are methyl in order to obtain an excellent transparency. The average value of \bar{a} is from 0.8 to 2.2, but is preferably from 1.95 to 2.05 to achieve excellent bonding.

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The molecular configuration of ingredient A can be straight chain, branch-containing straight chain, cyclic, network or three-dimensional, however a straight-chain structure, possibly with a very small quantity of branching, is preferred. The molecular weight of this component is not particularly limited, and may range from that of a low-viscosity liquid to that equivalent to a very high-viscosity gum. The viscosity of this ingredient component is preferably 0.05 to 100 Pa.s, measured at 25°C from a consideration of the workability of the composition in mixing and bonding.

40

Examples of polyorganosiloxanes suitable as ingredient A include but are not limited to polyvinylsiloxane, vinylsiloxane-methylsiloxane copolymers, dimethylvinylsiloxane-terminated polydimethylsiloxanes, dimethylvinylsiloxane-terminated dimethylsiloxane-methylphenylsiloxane copolymers, dimethylvinylsiloxane-terminated dimethylsiloxane-methylvinylsiloxane copolymers, dimethylvinylsiloxane-terminated dimethylsiloxane-diphenylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxane-terminated dimethylsiloxane-methylvinylsiloxane copolymers, trimethylsiloxane-terminated dimethylsiloxane-methylphenylsiloxane-methylvinylsiloxane copolymers, dimethylvinylsiloxane-terminated polymethyl(3,3,3-trifluoropropyl) siloxanes, dimethylvinylsiloxane-terminated dimethylsiloxane-methyl(3,3,3-trifluoropropyl)siloxane copolymers and polysiloxanes composed of $\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$ units, $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units.

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The combination of a dimethylvinylsiloxane-terminated polydiorganosiloxane with a polysiloxane composed of $\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$ units, $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units can be used as ingredient A when an increased strength is sought for the cured product of the present polyorganosiloxane compositions.

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Ingredient B is the crosslinking agent for ingredient A. The silicon-bonded hydrogen atoms of this ingredient participate in an addition reaction with the lower alkenyl radicals ingredient A under the catalytic

activity of ingredient C in order to cure the composition. The organic groups bonded to silicon are typically monovalent hydrocarbon radicals, and preferred examples are as enumerated for R above, with the exception of alkenyl radicals. The molecular configuration of the organohydrogensiloxane is not particularly restricted and it may be straight chain, branch-containing straight chain or cyclic. The molecular weight of this ingredient is likewise not particularly restricted, however the viscosity is preferably from about 0.001 to about 50 Pa.s at 25°C to obtain an excellent miscibility with ingredient A. The concentration of this ingredient in the present compositions is determined by the condition that the molar ratio of the total quantity of silicon-bonded hydrogen atoms of this ingredient relative to the total quantity of alkenyl groups in ingredients A and D is from 0.5 to 3, inclusive. When this molar ratio is less than 0.5, an excellent curability will not be obtained. When this ratio exceeds 3.0 the resulting composition tends to foam easily.

When the aforementioned vinyl-containing polysiloxane is additionally employed for reinforcement or other purposes, additional organohydrogensiloxane must be present to maintain the required molar ratio of silicon bonded hydrogen to alkenyl radicals in the composition.

Specific examples of the organohydrogensiloxane ingredient include but are not limited to trimethylsiloxyl-terminated polymethylhydrogensiloxanes, trimethylsiloxyl-terminated dimethylsiloxane-methylhydrogensiloxane copolymers, dimethylhydrogensiloxyl-terminated polymethylhydrogensiloxanes, dimethylhydrogensiloxyl-terminated dimethylsiloxanemethylhydrogensiloxane copolymers, dimethylsiloxane-methylhydrogensiloxane cyclic copolymers, copolymers composed of $(\text{CH}_3)_2\text{HSiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units and copolymers composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units, $(\text{CH}_3)_2\text{HSiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units.

Ingredient C catalyzes the addition reaction of silicon-bonded hydrogen atoms with alkenyl radicals and its concrete examples include chloroplatinic acid, alcohol and ketone solutions of chloroplatinic acid, aged alcohol and ketone solutions of chloroplatinic acid, chloroplatinic acid-olefin complexes, chloroplatinic acid-alkenylsiloxane complexes, platinum-diketone complexes, platinum black and supported platinum.

The concentration of ingredient C is equivalent to from 0.1 to 100 ppm of platinum metal based on the combined weight quantity of ingredients A, B, C and D. The crosslinking reaction will not proceed adequately at below 0.1 ppm of platinum in the composition. The use of more than 100 ppm of platinum is uneconomical and also significantly reduces the working time of the present curable compositions at room temperature. The platinum concentration is typically from about 1 to about 20 ppm.

The presence of ingredient D distinguishes the present compositions from prior art materials. This ingredient is responsible for the excellent bonding to substrates with which the present compositions are in contact with during curing.

Part (a) of ingredient D is a polysiloxane with a three-dimensional structure in which the basic structural unit is the $\text{SiO}_{4/2}$ unit. This unit is bonded through its oxygen atoms to the $\text{CH}_2 = \text{CH}(\text{R}^1)_2\text{Si}$, R^2_3Si and R^3 groups. This ingredient contains fewer than 30 $\text{SiO}_{4/2}$ units because above this limit the molecular weight is too large for the ingredient to impart the required adhesion to the composition. The number of $\text{SiO}_{4/2}$ units is preferably about 20 from the standpoint of the miscibility of this ingredient with ingredient A, but must be at least 3 to prevent volatilization of part (a) during degassing of the composition.

The values represented by \underline{b} and \underline{d} in the formula for part (a) are both at least 1 because an excellent adhesion cannot be generated when these values are less than 1. The value of \underline{c} can be 0 or greater, the value of $(\underline{b} + \underline{c})/\underline{d}$ is from 0.2 to 2, and the value represented by $(\underline{b} + \underline{c} + \underline{d})/\underline{e}$ must be from 0.4 to 4. The reason for these limits is that excellent adhesion cannot be imparted when these values fall outside the specified ranges. It has been found that a composition in which $(\underline{b} + \underline{c} + \underline{d})/\underline{e}$ exceeds 4 essentially cannot be produced. R^1 , R^2 and R^3 are individually identical or different monovalent hydrocarbon radicals containing from 1 to 3 carbon atoms, with the proviso that these radicals do not contain ethylenic unsaturation. R^1 and R^2 are preferably methyl and R^3 is preferably methyl or ethyl.

Part (b) of ingredient D is an alkoxysilane containing at least one epoxide group. Specific examples of this ingredient include but are not limited to gamma-glycidoxypolytrimethoxysilane, gamma-glycidoxypolydimethoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane and 3,4-epoxycyclohexylethylmethyldimethoxysilane.

Part (a) of ingredient D can be synthesized by methods known in the art. An example of such a method is the cohydrolysis of 1 or more of dimethylvinylchlorosilane, dimethylvinylacetoxysilane, dimethylvinylethoxysilane, divinyltetramethyldisiloxane, trimethylchlorosilane, trimethylacetoxysilane and hexamethyldisiloxane with methyl orthosilicate or ethyl orthosilicate in the presence of a strictly regulated quantity of water. It is recommended that an acid catalyst such as hydrochloric acid be employed in this cohydrolysis. Each silicon compound used in this cohydrolysis can be a mixture of 2 or more species.

A compound corresponding to part (a) produced as described hereinbefore may contain residual silanol groups and, after mixing with part (b), an alcohol-releasing reaction may be conducted in the presence of an alkali catalyst such as sodium hydroxide, potassium hydroxide or potassium silanolate. During the prepara-

tion of ingredient D, part (a) may be partially reacted with part (b), or a simple mixture of these two parts may be used.

When the alkali-catalyzed alcohol releasing reaction is performed, the mixture present following the reaction is preferably neutralized with, for example, carbon dioxide, a chlorosilane or acetic acid, before use.
 5 The weight ratio of part (a) to part (b) in ingredient D must be within the range of 0.1 to 10, and preferably within the range of from 0.5 to 2 in order to obtain good adhesion between the cured composition of this invention and the substrate.

The weight of ingredient D must not exceed 1/5 of the weight of ingredient A because the addition of larger quantities degrades the properties of the composition itself. The optimal quantity of ingredient D for
 10 obtaining excellent adhesion will depend on the structures of the other components, but it is approximately from 1 to 8 parts by weight of ingredient D per 100 parts by weight of ingredient A.

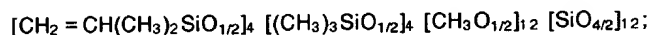
The curable polyorganosiloxane compositions of the present invention can be produced by simply mixing ingredients A, B, C, and D using any mixing apparatus suitable for mixing a fluid or gum. Examples of suitable mixing devices include planetary mixers, screw mixers, static mixers and kneader mixers.

15 It is recommended that a small or very small amount of an additive, such as acetylene compounds, hydrazines, triazoles, phosphines and mercaptans, be added to the curable polyorganosiloxane composition of the present invention in order to inhibit the curing reaction at room temperature. In addition, fillers such as fine silica powder and carbon black, thermal stabilisers, colorants and flame retardants may optionally be added unless they adversely affect achieving the objectives of the present invention, specifically a curable
 20 composition exhibiting excellent adhesion to a variety of substrates.

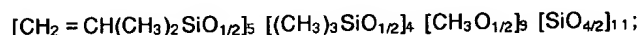
The following examples describe preferred embodiments of the present compositions and should not be interpreted as limiting the scope of the accompanying claims. All parts and percentages in the examples are by weight unless otherwise specified, and viscosity and other properties are measured at 25 °C.

25 Example 1

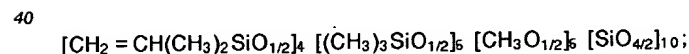
A series of polyorganosiloxane compositions were prepared from a dimethylvinylsiloxy-terminated polydimethylsiloxane with a viscosity of 2 Pa.s (polymer A1); a trimethylsiloxy-terminated copolymer consisting essentially of dimethylsiloxane and methylhydrogensiloxane units in a molar ratio of 3:5,
 30 respectively, and exhibiting a viscosity of 0.01 Pa.s (polymer XI); a 1% by weight solution of chloroplatinic acid in 2-ethylhexanol (catalyst 1); a polysiloxane (polymer M1) with the formula



35 a polysiloxane (polymer M2) with the formula



a polysiloxane (polymer M3) with the formula



gamma-glycidioxypropyltrimethoxysilane (silane 1); the reaction product (polymer M4) obtained by heating a 1:1 weight ratio mixture of polymer M1 and silane 1 at 100 °C for 1 hour in the presence of 500 ppm KOH, removing the produced methanol and neutralizing the reaction mixture with Me₃SiCl; the reaction mixture
 45 (polymer M5) obtained by heating a 1:1 weight ratio mixture of polymer M2 and silane 1 at 100 °C for one hour in the presence of 500 ppm KOH; and 3-methylbutyne-3-ol (additive I1). Each composition was cured in contact with glass at 150 °C. The light transmission and adhesion to glass of the cured products were measured and the results are reported in Table 1. The adhesion values reported in Table 1 are the %
 50 cohesive failure, i.e. the percent of substrate surface to which the cured elastomer had adhered. The curing time is the time required for a complete curing of the composition. Light transmission was measured at a wavelength of 500 nm on a 10 mm thickness of the cured product.

TABLE 1

Ingredients	Comparative example 1		Experiment number				
	2	3	4	5	6	7	8
polymer A1 (parts)	100	100	100	100	100	100	100
polymer X1 (parts)	1.8	1.8	1.8	1.8	1.8	1.8	1.8
catalyst 1 (parts)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
additive I1 (parts)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
polymer M1 (parts)	1.5	1.5					
polymer M2 (parts)			1.5				
polymer M3 (parts)				2.0	1.0		
polymer M4 (parts)						3.0	
polymer M5 (parts)							3.0
silane 1 (parts)	1.5	1.0	1.5	1.0	2.0		
light transmission (%)	98	98	98	97	98	98	98
curing time (minutes @150°C)	3	3	3	3	3	3	3
Cohesive Failure (%)	60	100	100	100	100	100	100

Example 2

A composition was prepared from 100 parts dimethylvinylsiloxyl-terminated polydimethylsiloxane with a viscosity of 10 Pa.s; 10 parts polyorganosiloxane resin with a vinyl group content of 1%, a softening point of 120°C and consisting essentially of dimethylvinylsiloxyl, trimethylsiloxyl and SiO_{4/2} units; 30 parts of trimethylsilyl-hydrophobicized fumed silica; 0.4 parts tetramethyltetravinylcyclotetrasiloxane; 10 parts of a trimethylsiloxyl-terminated copolymer consisting essentially of dimethylsiloxane and methylhydrogensiloxane units in a molar ratio of 3:1, respectively, and exhibiting a viscosity of 0.01 Pa.s; and a divinyltetramethyl-disiloxane-chloroplatinic acid complex in an amount equivalent to 10 ppm platinum, based on the weight of the total composition. These ingredients are combined and blended with one of the adhesion promoters from Example 1, in the quantity specified in Table 2, followed by degassing at room temperature under reduced pressure for 30 minutes. The compositions were then applied to various substrates and cured at 120°C for 30 minutes. The percent cohesive failure was measured for each substrate and the results reported in Table 2. In the table, the concentrations of the adhesion promoters are expressed in parts by weight, based on 100 parts of the polydimethylsiloxane.

Table 2

Example No.	9*	10	11	12
	Adhesion Promoters			
	A	B	C	D
<u>Substrates</u>				
iron	50	95	50	50
stainless steel	50	95	50	50
copper	100	100	100	100
aluminum	100	100	100	100
phenol resin	100	100	100	100
polyethylene terephthalate resin	100	100	100	100
epoxy resin	0	100	100	100
polybutylene terephthalate resin	100	100	100	100
polymethyl methacrylate resin	50	100	100	100
polyphenylene sulfide resin	0	100	100	100

Adhesion Promoters: A - 3 parts polymer M1 (Ex.1)
 B - 3 parts of a 1:1 weight ratio mixture of polymer M1 and silane 1
 C - 3 parts polymer M4
 D - 3 parts polymer M5

* - Comparative Example

The foregoing data demonstrate that the addition of the present adhesion promoters to an addition-curable polyorganosiloxane composition imparts excellent adhesion without adversely affecting other desirable properties such as rate of the curing reaction, transparency. In addition there is no reduction in adhesion following degassing of the composition. The compositions therefore exhibit excellent adhesion to substrates, in particular, organic resins, which are in contact with the composition during curing.

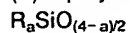
Accordingly, the curable polyorganosiloxane compositions of this invention are suitable as adhesives or coating materials for diverse substrates, for example, glass, ceramics, metals, resins, papers and textiles. The compositions are useful in various industries such as the electric/electronic industry, the measurement instrument industry, the automobile industry, the machine industry, in civil engineering and construction and in the container, packaging and medical appliance industries.

In addition, the composition is highly transparent and so is optimal as an adhesive in optical applications.

Claims

1. A curable composition comprising:

(A) a polyorganosiloxane with the average unit formula

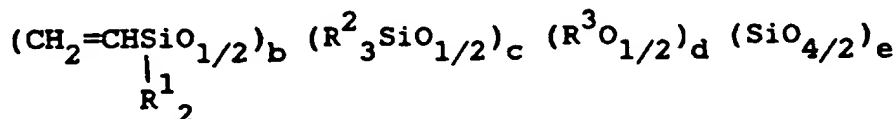


containing an average of at least two radicals per molecule, selected from the group consisting of vinyl, allyl, propenyl where R represents a monovalent hydrocarbon group, a haloalkyl group, hydroxy group or the above-mentioned alkenyl radicals and the value of a is from 0-8 to 2.2;

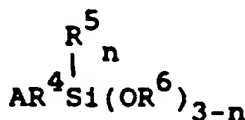
(B) an organohydrogensiloxane containing at least 2 silicon-bonded hydrogen atoms per molecule and no alkenyl groups, where the concentration of (B) is sufficient to provide a molar ratio of silicon bonded hydrogen atoms relative to the total moles of alkenyl groups present in ingredients A and D of from 0.5 to 3.0.

(C) a amount of a platinum-type catalyst equivalent to from 0.1 to 100 ppm of platinum metal, based on the combined quantities of ingredients (A), (B) and (C); and

(D) an adhesion promotor characterized in that the adhesion promotor (D) is a mixture or reaction product of (a) a polysiloxane corresponding to the average formula



where R^1 , R^2 and R^3 represent identical or different monovalent hydrocarbon radicals other than alkenyl radicals and contain from 1 to 3 carbon atoms, b and d are at least 1, c is 0 or greater, the value of $(b + c)/d$ is from 0.2 to 2, the value of $(b + c + d)/e$ is from 0.4 to 4 and e is from 3 to 30 and (b) an alkoxysilane of the formula



where A represents a glycidoxy or epoxycyclohexyl group, R^4 represents a divalent hydrocarbon radical containing from 1 to 3 carbon atoms, R^5 and R^6 represent identical or different monovalent hydrocarbon radicals other than alkenyl and contain from 1 to 3 carbon atoms, and n is 1 or 0, and where the weight ratio of (a) to (b) is from 0.1 to 10, inclusive and the weight ratio of (D) relative to (A) does not exceed 0.2.

2. A composition according to claim 1 where R is alkyl, aryl, haloalkyl or alkenyl, the hydrocarbon radicals present in (B) are alkyl, aryl or haloalkyl, the molar ratio of silicon bonded hydrogen atoms to alkenyl radicals in said composition is from 0.5 to 3.0, inclusive, R^1 and R^2 are methyl and R^3 is methyl or ethyl.
3. A composition according to claim 2 where R is methyl or 3,3,3- trifluoropropyl, the alkenyl radicals are vinyl, and part (b) of ingredient D is selected from the group consisting of gamma-glycidoxypropyltrimethoxysilane, gamma- glycidoxypropylmethyldimethoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane, and 3,4-epoxycyclohexylethylmethyldimethoxysilane.
4. A composition according to claim 3 where at least 70 percent of the R radicals are methyl, e is no more than 20, the composition contains from 1 to 8 parts by weight of (D) per 100 parts of (A), and the weight ratio of part (a) of ingredient (D) to part (b) of ingredient (D) is from 0.5 to 2.
5. A composition according to claim 4 where at least 90 percent of the radicals represented by R are methyl, the value of a is from 1.95 to 2.05, the viscosity of (A) is from 0.05 to 100 Pa.s at 25°C the viscosity of (B) is from 0.001 to 50 Pa.s at 25°C the concentration of said catalyst is equivalent to from 1 to 20 ppm of platinum, based on the combined weight of A, B, C and D, the composition contains a polysiloxane composed of of $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$, $(\text{CH}_3)_3\text{SiO}_{1/2}$ and $\text{SiO}_{4/2}$ units, and a platinum catalyst inhibitor.
6. A composition according to claim 5 where the platinum catalyst is chloroplatinic acid, b is 4 or 5, c is 4, 5, or 6, the value of d is from 6 to 12, inclusive, the value of e is 10, 11 or 12, part (b) of ingredient (D) is gamma- glycidoxypropyltrimethoxysilane and the weight ratio of part (a) to part (b) of ingredient (D) is 1:1.

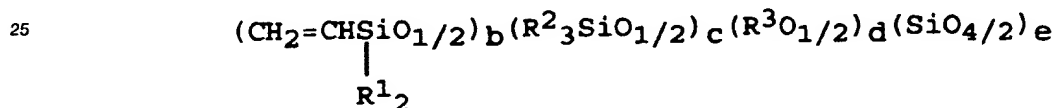
7. A composition according to claim 6 where ingredient (D) is a reaction product of part (a) and part (b) of ingredient (D).
8. A composition according to claim 7 where said composition contains fume silica as a filler.

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Patentansprüche

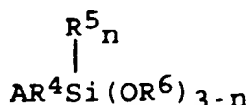
1. Härtbare Zusammensetzung umfassend

- (A) ein Polyorganosiloxan mit der durchschnittlichen Einheitsformel
- 10 $R_aSiO_{(4-a)/2}$,
das durchschnittlich mindestens zwei Reste ausgewählt aus der Gruppe bestehend aus Vinyl-, Allyl-, Propenylresten pro Molekül enthält, wobei R eine monovalente Kohlenwasserstoffgruppe, eine Halogenalkylgruppe, eine Hydroxygruppe oder die oben erwähnten Alkenylreste bedeutet und der Wert von a 0,8 bis 2,2 ist;
- 15 (B) ein Organohydrogensiloxan, das mindestens zwei siliziumgebundene Wasserstoffatome pro Molekül und keine Alkenylgruppen enthält, wobei die Konzentration von (B) ausreichend ist, um ein molares Verhältnis von siliziumgebundenen Wasserstoffatomen zu der Gesamtanzahl Mol Alkenylgruppen, die in den Inhaltsstoffen A und D vorhanden ist, von 0,5 bis 3,0 bereitzustellen
- (C) eine Menge eines platinhaltigen Katalysators, die 0,1 bis 100 ppm Platinmetall äquivalent ist, bezogen auf die vereinigten Mengen der Inhaltsstoffe (A), (B) und (C) und
- 20 (D) einen Haftvermittler, dadurch gekennzeichnet, daß der Haftvermittler (D) eine Mischung oder ein Reaktionsprodukt von (a) einem Polysiloxan der durchschnittlichen Formel



- 30 worin R^1 , R^2 und R^3 identische oder verschiedene andere monovalente Kohlenwasserstoffreste als Alkenylreste bedeuten, die 1 bis 3 Kohlenstoffatome enthalten, b und d mindestens 1 sind, c 0 oder größer ist, der Wert von $(b+c)/d$ 0,2 bis 2 ist, der Wert von $(b+c+d)/e$ 0,4 bis 4 ist und e 3 bis 30 ist und (b) einem Alkoxysilan der Formel

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- worin A eine Glycidoxy- oder Epoxycyclohexylgruppe bedeutet, R^4 einen divalenten Kohlenwasserstoffrest mit 1 bis 3 Kohlenstoffatomen bedeutet, R^5 und R^6 identische oder verschiedene andere monovalente Kohlenwasserstoffreste als Alkenylgruppen bedeuten, die 1 bis 3 Kohlenstoffatome enthalten und n 1 oder 0 ist und worin das Gewichtsverhältnis von (a) zu (b) 0,1 bis einschließlich 10 ist und das Gewichtsverhältnis von (D) zu (A) 0,2 nicht übersteigt.
- 45

2. Zusammensetzung nach Anspruch 1, worin R ein Alkyl-, Aryl-, Halogenalkyl- oder Alkenylrest ist, die in (B) vorhandenen Wasserstoffreste Alkyl-, Aryl- oder Halogenalkylreste sind, das molare Verhältnis von siliziumgebundenen Wasserstoffatomen zu Alkenylresten in der Zusammensetzung 0,5 bis einschließlich 3,0 ist, R^1 und R^2 Methylreste sind und R^3 ein Methyl- oder Ethylrest ist.
- 50

3. Zusammensetzung nach Anspruch 2, worin R ein Methyl- oder 3,3,3-Trifluorpropylrest ist, die Alkenylreste Vinylreste sind und Teil (b) von Inhaltsstoff (D) ausgewählt ist aus der Gruppe bestehend aus gamma-Glycidoxypropyltrimethoxysilan, gamma-Glycidoxypropylmethyldimethoxysilan, 3,4-Epoxycyclohexylethyltrimethoxysilan und 3,4-Epoxycyclohexylethylmethyldimethoxysilan.
- 55

4. Zusammensetzung nach Anspruch 3, worin mindestens 70% der Reste R Methylreste sind, e nicht größer als 20 ist, die Zusammensetzung 1 bis 8 Gewichtsteile (D) pro 100 Teile (A) enthält und das

Gewichtsverhältnis von Teil (a) von Inhaltsstoff (D) zu Teil (b) von Inhaltsstoff (D) 0,5 bis 2 ist.

5. Zusammensetzung nach Anspruch 4, worin mindestens 90% der durch R dargestellten Reste Methylreste sind, der Wert von a 1,95 bis 2,05 ist, die Viskosität von (A) 0,05 bis 100 Pa·s bei 25 °C ist, die Viskosität von (B) 0,001 bis 50 Pa·s bei 25 °C ist, die Konzentration des Katalysators gleich ist 1 bis 20 ppm Platin, bezogen auf das vereinigte Gewicht von A, B, C und D, die Zusammensetzung ein Polysiloxan, das aus $\text{CH}_2=\text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$, $(\text{CH}_3)_3\text{SiO}_{1/2}$ und $\text{SiO}_{4/2}$ - Einheiten zusammengesetzt ist und einen Inhibitor für den Platinkatalysator enthält.
6. Zusammensetzung nach Anspruch 5, worin der Platinkatalysator Chlorplatinsäure ist, b 4 oder 5 ist, c 4, 5 oder 6 ist, der Wert von d 6 bis einschließlich 12 ist, der Wert von e 10, 11 oder 12 ist, Teil (b) von Inhaltsstoff (D) gamma-Glycidoxypropyltrimethoxysilan ist und das Gewichtsverhältnis von Teil (a) zu Teil (b) von Inhaltsstoff (D) 1:1 ist.
7. Zusammensetzung nach Anspruch 6, worin Inhaltsstoff (D) ein Reaktionsprodukt von Teil (a) und Teil (b) von Inhaltsstoff (D) ist.
8. Zusammensetzung nach Anspruch 7, worin die Zusammensetzung gebranntes Siliziumdioxid als Füllstoff enthält.

Revendications

1. Composition durcissable comprenant :

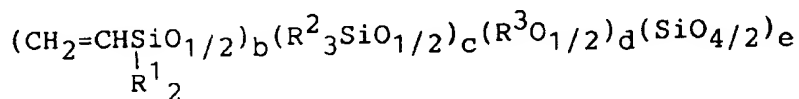
(A) un polyorganosiloxane ayant la formule unitaire moyenne :

$\text{R}_a\text{SiO}_{(4-a)/2}$ contenant en moyenne au moins deux radicaux par molécule, choisis dans l'ensemble constitué par les radicaux vinyle allyle et propényle, où R représente un groupe hydrocarboné monovalent, un groupe halogénoalkyle, un groupe hydroxy ou les radicaux alkényles indiqués ci-dessus, et la valeur de a est de 0,8 à 2,2 ;

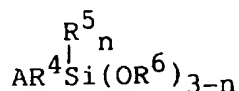
(B) un organohydrogénosiloxane contenant au moins 2 atomes d'hydrogène liés au silicium par molécule, et pas de groupe alkényle, où la concentration de (B) est suffisante pour fournir un rapport molaire des atomes d'hydrogène liés au silicium au nombre total de moles de groupes alkényles présents dans les ingrédients A et D de 0,5 à 3,0 ;

(C) un catalyseur du type platine en une quantité équivalente à 0,1 à 100 ppm de platine métallique, par rapport aux quantités combinées des ingrédients (A), (B) et (C); et

(D) un promoteur d'adhérence, caractérisée en ce que ledit promoteur d'adhérence (D) est un mélange ou un produit de réaction de (a) un polysiloxane correspondant à la formule moyenne :



où R^1 , R^2 et R^3 représentent des radicaux hydrocarbonés monovalents identiques ou différents les uns des autres, autres que des radicaux alkényles, et contiennent de 1 à 3 atomes de carbone, b et d valent au moins 1, c vaut 0 ou plus, la valeur de $(b + c)/d$ est de 0,2 à 2, la valeur de $(b + c + d)/e$ est de 0,4 à 4, et e vaut de 3 à 30, et (b) un alcoxysilane de formule :



où A représente un groupe glycidoxy ou époxycyclohexyle, R^4 représente un radical hydrocarboné bivalent contenant de 1 à 3 atomes de carbone, R^5 et R^6 représentent des radicaux hydrocarbonés monovalents identiques ou différents, autres que des radicaux alkényles, et contiennent de 1 à 3 atomes de carbone, et n vaut 1 ou 0, où le rapport pondéral de (a) à (b) vaut de 0,1 à 10 inclus, et

le rapport pondéral de (D) à (A) ne dépasse pas 0,2.

2. Composition selon la revendication 1, où R est un groupe alkyle, aryle, halogénoalkyle ou alkényle, les radicaux hydrocarbonés présents dans (B) sont des groupes alkyles, aryles ou halogénoalkyles, le rapport molaire des atomes d'hydrogène liés au silicium aux radicaux alkényles dans ladite composition vaut de 0,5 à 3,0 inclus, R¹ et R² sont des groupe méthyles, et R³ est un groupe méthyle ou éthyle.
3. Composition selon la revendication 2, où R est un groupe méthyle ou 3,3,3-trifluoropropyle, les radicaux alkényles sont des radicaux vinyle, et la partie (b) de l'ingrédient D est choisie dans l'ensemble constituée par les gamma-glycidoxypropyltriméthoxysilane, gamma-glycidoxypropylméthyltriméthoxysilane, 3,4-époxy-cyclohexyléthyltriméthoxysilane et 3,4-époxy-cyclohexyléthylméthyltriméthoxysilane.
4. Composition selon la revendication 3, où au moins 70 % des radicaux R sont des radicaux méthyle, e ne vaut pas plus de 20, la composition contient 1 à 8 parties en poids de (D) pour 100 parties de (A), et le rapport pondéral de la partie (a) de l'ingrédient (D) à la partie (b) de l'ingrédient (D) vaut de 0,5 à 2.
5. Composition selon la revendication 4, où au moins 90 % des radicaux représentés par R sont des radicaux méthyle, la valeur de a est de 1,95 à 2,05, la viscosité de (A) est de 0,05 à 100 Pa.s à 25 °C, la viscosité de (B) est de 0,001 à 50 Pa.s à 25 °C, la concentration dudit catalyseur équivaut à 1 à 20 ppm de platine, sur la base du poids combiné de A, B, C et D, la composition contient un polysiloxane composé d'unités $\text{CH}_2 = \text{CH}(\text{CH}_3)_2\text{SiO}_{1/2}$, d'unités $(\text{CH}_3)_3\text{SiO}_{1/2}$ et d'unités $\text{SiO}_{4/2}$, et un inhibiteur du catalyseur du type platine.
6. Composition selon la revendication 5, où le catalyseur du type platine est l'acide chloroplatinique, b vaut 4 ou 5, c vaut 4, 5 ou 6, d vaut de 6 à 12 inclus, e vaut 10, 11 ou 12, la partie (b) de l'ingrédient (D) est un gammaglycidoxypropyltriméthoxysilane, et le rapport pondéral de la partie (a) à la partie (b) de l'ingrédient (D) vaut 1:1.
7. Composition selon la revendication 6, où l'ingrédient (D) est un produit de réaction de la partie (a) et de la partie (b) de l'ingrédient (D).
8. Composition selon la revendication 7, où ladite composition contient de la silice de fumée comme charge.